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# review

OF RECENT  
DEVELOPMENTS

## Oxidation-Resistant Coatings for Refractory Metals

B. C. Allen • January 28, 1970

### COATING DEVELOPMENT

The investigation of the oxidation behavior and tensile properties of hafnium-base alloys containing tantalum plus other minor additions has continued at IIT Research Institute.<sup>(1)</sup> The intended use for such alloys lies in structural components or claddings for other refractory metals. Cyclic oxidation tests were conducted on the three most oxidation-resistant alloys developed in previous programs. Weight-gain curves for all three alloy variations were similar; they were linear from 1200 to 1800 F and parabolic from 2000 to 2700 F. Typical results are presented in Figure 1. Scale-growth behavior of the three alloys was also similar, as indicated in Figure 2. The change from linear to parabolic oxidation was the result of precipitation of the alpha hafnium phase from the beta matrix caused by oxygen, followed by preferential oxidation of the alpha-rich areas. The resulting subscale provided a buffer to stresses caused by expansion mismatch of the surface oxide and substrate. Since the length of thermal cycle used (2 and 12 hours) gave essentially the same results, oxidation life apparently was not affected by cycling through the temperature range of linear oxidation. Preoxidation for 10 to 20 hours at 2500 F permitted exposure of the alloys, generally up to 100 hours at 1200 to 1800 F, with almost no measurable weight gain. The solidus of the three alloys ranged between 3000 and 3100 F compared with 3900 F for the Hf-25Ta binary alloy.

Extrapolation of IIT Research Institute test results indicated that an expected life for a 20-mil-thick cladding would be about 1000, 300, and 100 hours at 2200, 2500, and 2700 F, respectively. A composite consisting of Ta-10W clad with 20 mils of Hf-24.5Ta-1.2Cr-0.66B-0.12Al survived 300 hours at 2500 F. The projected life thus was essentially realized in the composite, although visible cracks were present in a welded-seam closure of the cladding after 20 hours of exposure.

According to a British investigation, boron-modified silicide coatings were more protective on Mo-0.5Ti alloy than the unmodified silicide, particularly under cyclic conditions.<sup>(2)</sup> Silicon and boron were deposited on alloy specimens, respectively, from gaseous  $\text{SiCl}_2$  and BF. The weight of boron deposited was nominally 10 percent of the silicon deposited. Isothermal air-oxidation resistance of the unmodified silicide 2 mils thick was nominally 700 hours at 2190 F. The resistance in 20-minute cycles from room temperature to 2190 F

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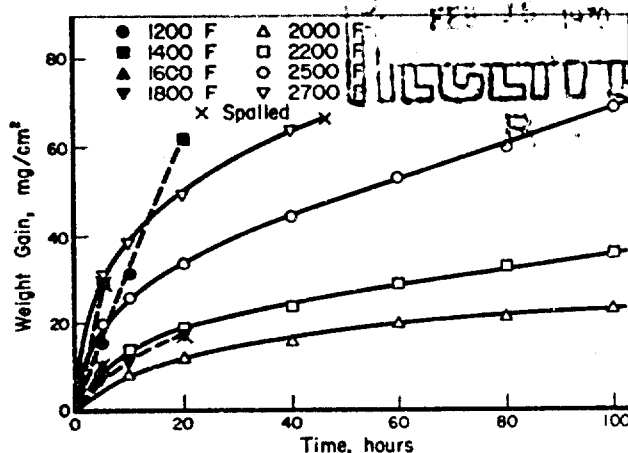


FIGURE 1. WEIGHT GAIN OF HOT-ROLLED Hf-24.5Ta-1.2Cr-0.66B-0.12Al ALLOY IN STATIC AIR<sup>(1)</sup>

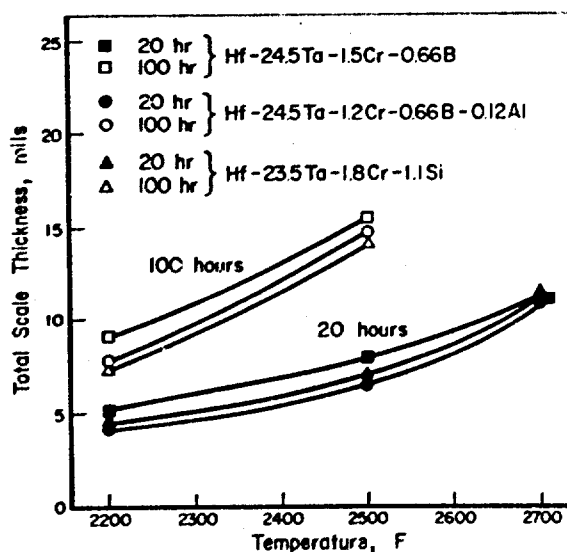


FIGURE 2. TOTAL SCALE THICKNESS DEVELOPED ON HAFNIUM-BASE ALLOYS IN STATIC AIR EXPOSURES AT 2200 TO 2700 F<sup>(1)</sup>

was 30 to 150 cycles. In comparison, the isothermal life of the boron-modified silicide was four times longer and the cyclic life was 50 times greater. On

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the basis of cyclic oxidation and pest oxidation tests in a simulated engine-exhaust environment, the modified coating had a lower life at 2010 F maximum temperature than at 2190 F. Specimens that failed in 2010 F tests showed that oxidation occurred through microcracks and pinholes in the coating. Specimens in 2190 F tests failed by diffusion consumption, resulting from the formation of the less oxidation-resistant  $\text{Mo}_5\text{Si}_3$  phase. On the basis of metallography, electron probe, and X-ray analysis, the beneficial effect of boron appears associated with the formation at 2190 F of a thermally stable cristobalite phase containing small amounts of boron and molybdenum. Miniature Charpy impact tests indicated that coated unnotched specimens behaved similarly to notched uncoated specimens by exhibiting brittle behavior up to 390 F.

Improved coatings are being developed by Sylvania Electric Products for columbium-alloy gas-turbine blades.<sup>(5)</sup> On the basis of cyclic-oxidation screening tests on Su-31 alloy (Cb-17W-3.5Hf-0.12C), a number of coatings have been selected for further evaluation. For example, Si-Fe-Cr fused-silicide coatings containing 20 to 25 percent iron and 20 to 25 percent chromium have given satisfactory protection for 500 hours at 2000 F and over 200 hours at 2200 F in static air. Ballistic impact damage on all candidate coatings prior to oxidation exposure for 10 hours at 2000 or 2200 F resulted in a locally contaminated substrate zone.

#### HARDWARE EVALUATION

An investigation of the feasibility of Sn-Al-Mo-coated Ta-10W alloy heat shields has been conducted at NASA/Langley.<sup>(4)</sup> No significant difference in cyclic oxidation life in static air at 2000 to 2900 F was found between small coupons coated with Sn-27Al-5.5Mo or Sn-27.5Al-6.9Mo. According to information presented in Figure 3, reduced coating life was found in the shorter cyclic exposures.

The life of both coatings as determined from 0.1-hour exposures in static air (see lower curve in Figure 3) was reduced by a factor of 4 to normally 0.5 hour under subsonic airstream conditions. Most significant was the catastrophic failure of leading-edge specimens from substrate ignition shortly after the first evidence of coating failure at and above 2600 F. Normally, autoignition of tantalum and its alloys does not occur at temperatures below about 3000 F. One consideration is that coating oxidation products or coating compounds present in the Sn-Al-Mo coating fluxed tantalum oxide, thereby permitting autoignition at lower temperatures.

Both the coating and oxidation exposure caused reductions in substrate ductility. For example, the elongation of 8-mil-thick Ta-10W alloy sheet was reduced from 20 to 10 percent by the coating and to 1 percent after 5 hours of exposure in static air at 2600 F. Ductility reduction was less severe in 25-mil-thick sheet.

Corrugated Sn-Al-Mo-coated Ta-10W heat-shield assemblies were prepared and could accommodate large temperature differences between shield and underlying structure with no loss of structural integrity. No coating damage was found along overlapping surfaces and edges on nested, curved shields after two cyclic exposures to 2600 F in static air.

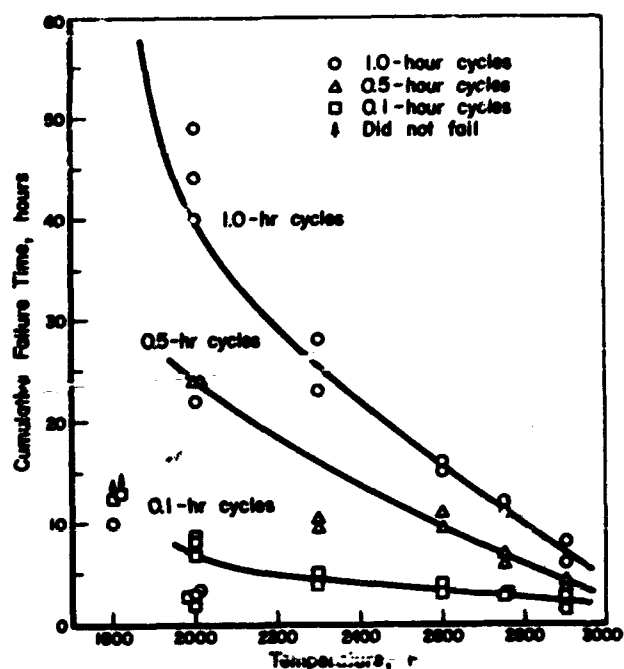


FIGURE 3. EFFECT OF TEMPERATURE AND CYCLIC EXPOSURE ON COATING LIFE OF Sn-27.5Al-6.9Mo-COATED Ta-10W COUPONS IN STATIC AIR<sup>(4)</sup>

Assemblies joined by resistance spot welds, heliarc spot welds, or rivets were tested, and general failure occurred in 9, 11, and 12 cycles totalling 2.7, 3.3, and 3.6 hours, respectively. These time periods were about one-half of those predicted from small-coupon data, caused probably by nonuniformities in the coating. Fusion between interlocking shields was not in evidence. Premature coating failures at the heat-shield plugs and access holes occurred at 2600 F and indicated that changes would be needed in design and/or fabrication methods to reduce frictional shear loading on the coating.

Pratt & Whitney has started a program to evaluate coated columbium alloys for use in aircraft gas-turbine engine burner-can-liner applications.<sup>(5)</sup> Failure modes were identified as oxidation-erosion, cracking, buckling, and burning. The corresponding material properties were oxidation erosion, thermal fatigue, creep, and melting. Four coated columbium-alloy systems were selected from preliminary screening. The substrates to be evaluated include PS-65, B-66, and C-129Y columbium; the coating candidates include Sylvania's RS12A (Si-20Cr-5Ti) and RS12B (Si-20Cr-20Fe).

#### REFERENCES

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- (4) Wichorek, G. R., and Stein, B. A., "Experimental Investigation of Aluminide-Coated Ta-10W for Heat-Shield Applications", Report NASA TN D-5524, NASA, Langley Research Center, Hampton, Va. (November 1969).
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